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<b>(54) Title:</b> COMPOSITIONS OF POLYPHENYLENE ETHER RESIN AND SYNDIOTACTIC POLYSTYRENE  <b>(57) Abstract</b>  The present invention provides a resin composition containing (A) a polyphenylene ether resin and (B) a syndiotactic styrene polymer, characterized in that (1) the composition also contains (C) a high-impact styrene resin; and (2) the composition contains (C) in the amount of 90-10 parts by weight with respect to 10-90 parts by weight of (A) and (B) in the amount of 5 to 60 parts by weight with respect to a total of 40 to 95 parts by weight of (A) and (C).		

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## DESCRIPTION

## COMPOSITIONS OF POLYPHENYLENE ETHER RESIN AND SYNDIOTACTIC POLYSTYRENE

## 5 FIELD OF THE INVENTION

The present invention concerns a resin composition containing a polyphenylene ether (abbreviated in the following as PPE) resin, and more specifically, it concerns a resin composition of the  
10 aforementioned type which is highly useful in plastic applications requiring chemical resistance in the field of industrial and household materials such as automotive components, electrical and electronic components, household materials for the kitchen, bathroom, and construction, and lavatory products.

## 15 PRIOR ART

As non-crystalline (amorphous) resins show outstanding dimensional accuracy in injection molding due to their amorphous structural properties, their properties are taken advantage of in widespread use in large-scale molded products and industrial fields  
20 requiring precision assembly, etc. However, because of their amorphous structure, they are permeable to organic chemicals, i.e., they show poor chemical resistance, and they therefore have the drawback of being easily attacked by substances such as oils and organic solvents.

On the other hand, due to their crystalline properties,  
25 crystalline resins show highly outstanding chemical resistance and are therefore used in applications involving contact with oils, organic solvents, etc., but when crystallization proceeds during the molding

cooling process, the phenomenon of molding shrinkage occurs, resulting in poor dimensional stability and making these resins unsuitable for large-scale molded products. In order to remedy this, attempts have been made to add inorganic fillers such as glass fibers, but this causes  
5 an increase in specific gravity and a decrease in ductile impact strength, as well as discrepancies in the degree of shrinkage in the direction of injection molding flow and perpendicular to this direction, resulting in the defects of warping and deformation.

Polyphenylene ether resin is a typical non-crystalline  
10 thermoplastic resin having an elevated softening point. It has balanced mechanical properties and outstanding electrical properties, its water absorption is low, and it shows favorable dimensional stability. In addition, polyphenylene ether resin shows extremely favorable compatibility with polystyrene resin, another non-crystalline  
15 thermoplastic resin, and it can easily be deformed. As resin compositions composed of PPE resin and styrene resin (referred to in the following as a PPE/PS resin composition) show outstanding molding workability and impact resistance (US Patent No. 3,383,435), they have conventionally been widely used in applications such as automotive  
20 components and electrical and electronic components. However, this type of PPE/PS resin composition is an amorphous resin, and as mentioned above, it does not show sufficient chemical resistance, particularly resistance to aromatic hydrocarbon solvents. For example, when the solvent comes into contact with sites subjected to strain or molding  
25 residual strain, crazing and cracks may develop from these sites, resulting in failure of the component. For this reason, use of these compositions in such applications has been limited. For example, their

use is avoided in external automotive components, engine room components, and cabin interiors of ships, to which waxes, machine oils/engine oils, rust-preventing agents, aromatic agents, etc., may adhere; components for office equipment, computer-related equipment, etc., to which lubricating oils for sliding, grease, or cleaners may adhere (such as internal parts, fan motor cases, and plastic chassis); home electronic and commercial electrochemical product components, to which salad oil, tempura oil, or other organic solvents may adhere; and components of electrical and electronic equipment used in environments exposed to oil and smoke or organic gases (such as factory environments and construction environments). This is considered to be a fundamental drawback derived from the fact that polyphenylene ether resin is non-crystalline.

There have been many attempts in the past to remedy this defect, but no one has as yet been successful in developing a technology for improving chemical resistance without impairing the properties of PPE/PS resin compositions. Examples from prior art include the methods of mixing the PPE/PS resin composition with crystalline resins such as polyolefins (e.g., polyethylene, polypropylene, EEA), polyester, nylon, etc.; low-molecular-weight olefins (such as polybutene and ethylene oligomer); or rubber-like polymers (such as SEBS, SBS, or SEPS rubber). In these technologies, however, although addition of small amounts does improve chemical resistance somewhat, when the amount added is increased in order to increase chemical resistance to the level required for practical use, this not only causes a reduction in the outstanding mechanical strength, thermal resistance, and flame resistance properties of conventional PPE/PS resin compositions, it

causes the phenomenon of laminar peeling during injection molding due to insufficient compatibility and impairs dimensional accuracy during molding.

In recent years, moreover, there have been numerous attempts  
5 involving the technology of alloying a crystalline resin with a  
non-crystalline thermoplastic resin, with a commercial example being  
the method of producing an alloy of polyphenylene ether resin and nylon  
resin during extrusion using a compatibilizer. In this method, the  
polyphenylene ether resin is finely mechanically dispersed in the nylon  
10 matrix, with this dispersion status controlled by means of the  
compatibilizer. The resulting product is referred to as a non-  
compatible alloy. Specifically, by covering the polyphenylene ether  
resin with a nylon matrix, the chemical permeability of the  
polyphenylene ether resin is inhibited, and its chemical resistance is  
15 improved. Looking at this from the nylon side, by dispersing the  
polyphenylene ether resin in the nylon, the poor dimensional stability  
resulting from shrinkage of the nylon during molding is improved, with  
this improvement increasing as an increasing amount of polyphenylene  
ether resin is mixed in. In this technology, however, the effect of  
20 improving dimensional stability resulting from the crystallinity of the  
nylon is insufficient.

In light of the above, a new technology allowing full  
compatibilization with polyphenylene ether resin and improved chemical  
resistance has been eagerly awaited.

25 Along with ground-breaking technological developments in recent  
years, crystalline styrene polymers having a syndiotactic  
stereostructure (referred to in the following as syndiotactic styrene

polymers) have been developed and manufactured commercially (Japanese Unexamined Patent Application No. S62-10481). As a natural result, there have been attempts to blend such syndiotactic styrene polymers with various resins.

- 5           There are known blended compositions of polyphenylene ether resins and syndiotactic styrene polymer which, because syndiotactic styrene resin is crystalline and has a styrene skeleton as the main component of its molecular structure, are expected to show favorable compatibility with polyphenylene ether resin in the same manner as
- 10 conventional atactic styrene polymers. Examples are presented in publications such as Japanese Unexamined Patent Applications H1-182344, H1-82350, H2-64140, H2-92948, H2-218724, H3-126743, H5-86296, H5-209098, H5-279530, H6-93151, H6-93153, H7-53815, H7-62175, H7-138433, H7-292184, H7-331003, H8-143699, H8-311196,
- 15 H9-52958, and H9-52959. Among the above publications, however, many of the compositions are simple alloys of syndiotactic styrene polymers and polyphenylene ether resins, and there are few concrete examples which clearly show an improvement in chemical resistance and a synergistic effect of the composition. The only publications in which
- 20 an improvement in chemical resistance is described are H2-64140, H2-92948, H9-52958, and H9-52959. In these publications, one simply adds a syndiotactic styrene polymer and an addition-type rubber-like elastic body to polyphenylene ether resin and attempts to increase chemical resistance by increasing the crystalline component, but as the
- 25 problem of maintaining the dimensional accuracy which is characteristic of amorphous polyphenylene ether resin is not taken into consideration, these compositions are ill-suited for practical application.

Furthermore, in all of these cases, chemical resistance is evaluated by the solvent immersion method, in which a molded test piece is immersed in a solvent and its external appearance is visually evaluated after a specified period of time, which is not an outstanding method from the standpoint of quantitative determination. As we have mentioned above, however, from the standpoint of the environment of use of polyphenylene ether resin, there are no applications in which the resin is constantly immersed in or in contact with a solvent. Due to the fact that components such as peripheral automotive engine parts and peripheral driving components of electrical and electronic devices are subject to adhesion of solvents, oils, etc., during use for several reasons, with fastening components, which are subjected to tightening strain, being particularly vulnerable to the problem of breakage, there are limitations on the use of these compositions in such applications, and in view of this fact, there is a demand for a polyphenylene ether resin which shows outstanding chemical resistance at sites subject to strain, i.e., does not develop crazing or cracks.

#### BRIEF DESCRIPTION OF THE INVENTION

The purpose of the present invention is to provide a PPE resin composition which has the chemical resistance required for practical applications while maintaining the high dimensional accuracy and other outstanding properties characteristic of polyphenylene ether resin.

The authors of the present invention studied the problem of how to inhibit crazing and cracking of polyphenylene ether resin at the aforementioned sites subjected to strain. The test method they used was to investigate chemical resistance by applying a solvent to a molded



product subjected to forced strain of 1% or more (a molded test piece was fixed in place on a die subjected to forced strain, the portion under strain was covered with a piece of gauze, etc., soaked in a solvent, and the extent of attack due to the solvent was evaluated), while  
5 simultaneously observing the polyphenylene ether resin from the twin standpoints of mechanical properties and stable dimensional accuracy. Surprisingly, they found that when a conventional crystalline polymer (syndiotactic styrene polymer) was added to a polyphenylene ether resin, it was not true that the effect of improving chemical resistance  
10 became greater as an increasing amount was added. Within a particular specified range, however, and when the combination included a high-impact styrene, an effect of improving chemical resistance was obtained while retaining the inherent properties of polyphenylene ether resin of outstanding dimensional accuracy and mechanical strength. In this  
15 manner, they arrived at the present invention.

The present invention provides a resin composition containing (A) a polyphenylene ether resin and (B) a syndiotactic styrene polymer, characterized in that

(1) the composition also contains (C) a high-impact styrene resin;  
20 and

(2) the composition contains (C) in the amount of 90-10 parts by weight with respect to 10-90 parts by weight of (A) and (B) in the amount of 5 to 60 parts by weight with respect to a total of 40 to 95 parts by weight of (A) and (C).

25 Conventionally, high-impact styrene resin has been blended in order to improve impact resistance, but when this styrene resin alone is added to polyphenylene ether resin, it has not had the effect of

improving the chemical resistance of the polyphenylene ether resin. Surprisingly, when high-impact styrene resin is blended into a system containing a syndiotactic styrene polymer and a polyphenylene ether resin, chemical resistance is further improved. Moreover, the fact that

5 syndiotactic styrene polymers cause a decrease in dimensional accuracy in systems in which the above range is exceeded and the fact that opacity and a decrease in physical properties of the composition occur due to excessive crystallinity were also not predicted based on prior art. Specifically, it was discovered that only when a syndiotactic styrene

10 polymer is blended with a polyphenylene ether in amounts exceeding the above range and a high-impact styrene resin is also blended into the composition is it possible to obtain a composition having both high dimensional accuracy and outstanding chemical resistance.

15 DESCRIPTION OF THE DRAWINGS

Fig. 1

Forced 1.5% bending strain die used in chemical resistance testing.

Fig. 2

20 Flat plate test piece measuring 100 mm x 100 mm x 3 mm used in measurement of molding shrinkage.

Explanation of Symbols

- a. Molding shrinkage flow direction
- b. Perpendicular to molding shrinkage flow direction

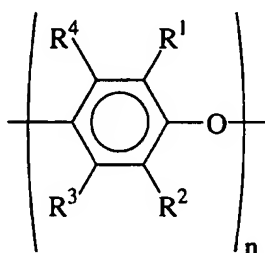
- 25
- 1. Gauze
  - 2. Solvent
  - 3. Specimen

4. Bent portion

5. Gate

#### DETAILED DESCRIPTION OF THE INVENTION

- 5        The (A) polyphenylene ether resin used in the resin composition of the present invention is known in and of itself, with this being a general term for a polymer having General Formula (I) below:



- In the formula, R¹, R², R³, and R⁴ are independent hydrogen atoms, halogen atoms, hydrocarbon groups, substituted hydrocarbon groups, alkoxy groups, cyano groups, phenoxy groups, or nitro groups, and n is an integer indicating the degree of polymerization), and polymers having the above general formula may be used either individually or in combinations of two or more in copolymers.

- 15        Specific examples of R¹, R², R³, and R⁴ are chlorine atoms, bromine atoms, iodine atoms, or methyl, ethyl, propyl, allyl, phenyl, benzyl, methylbenzyl, chloromethyl, bromomethyl, cyanoethyl, cyano, methoxy, ethoxy, phenoxy, or nitro groups.

- A preferred PPE resin is a polymer in which R¹ and R² in Formula (I) above are alkyl groups having 1-4 carbon atoms, and R³ and R⁴ are hydrogen or alkyl groups having 1-4 carbon atoms. n should preferably be 50 or a higher integer.

Specific examples include poly(2,6-dimethyl-1,4-phenylene)ether, poly(2,6-diethyl-1,4-phenylene)ether, poly(2-methyl-6-ethyl-1,4-phenylene)ether, poly(2-methyl-6-propyl-1,4-phenylene)ether, poly(2,6-dipropyl-1,4-phenylene)ether, poly(2-ethyl-6-propyl-1,4-phenylene)ether, poly(2,6-dimethoxy-1,4-phenylene)ether, poly(2,6-dichloromethyl-1,4-phenylene)ether, poly(2,6-dibromomethyl-1,4-phenylene)ether, poly(2,6-diphenyl-1,4-phenylene)ether, poly(2,6-ditolyl-1,4-phenylene)ether, poly(2,6-dichloro-1,4-phenylene)ether, poly(2,6-dibenzyl-1,4-phenylene)ether, and poly(2,5-dimethyl-1,4-phenylene)ether. Among these, a particularly preferred PPE is poly(2,6-dimethyl-1,4-phenylene)ether.

Moreover, an example of a PPE copolymer is a copolymer containing a portion of an alkyl tri-substituted phenol such as 2,3,6-trimethylphenol in the aforementioned polyphenylene ether repeating unit.

These PPE resins may also be copolymers with styrene compounds grafted on. An example of a styrene compound-grafted polyphenylene ether is a copolymer obtained by grafting a styrene compound such as styrene,  $\alpha$ -methylmethylstyrene, vinyl toluene, or chlorostyrene onto the aforementioned PPE resin and then carrying out graft polymerization.

Furthermore, the PPE resin may also be modified using a modifier having a polar group. Examples of polar groups include acid hydrides, carbonyl groups, acid anhydrides, acid amides, carboxylic esters, acid azides, sulfone groups, nitrile groups, cyano groups, isocyanate esters, amino groups, imide groups, hydroxyl groups, epoxy groups, oxazoline groups, and thiol groups.

The syndiotactic styrene polymer of component (B) of the present invention is a styrene polymer having a highly syndiotactic structure. A syndiotactic structure refers to a stereostructure in which phenyl groups or substituted phenyl groups are configured in mutually opposite  
5 directions with respect to a main chain composed of carbon-carbon bonds, and the tacticity thereof is determined by nuclear magnetic resonance using isotopic carbon ( $^{13}\text{C}$ -NMR). Tacticity as measured by  $^{13}\text{C}$ -NMR can be expressed by the number of multiple contiguous structural units, e.g., diad in the case of 2, triad in the case of 3, and pentad in the  
10 case of 5. In the present invention, the syndiotacticity of the styrene polymer is ordinarily characterized by a diad ratio of 75% or more, and preferably 85% or more, and a racemic pentad ratio of 30% or more, and preferably 50% or more. Examples of styrene polymers include polystyrene, poly(alkylstyrene), poly(halostyrene),  
15 poly(alkoxystyrene), poly(vinylbenzoic acid ester), mixtures thereof, or copolymers having these as their main components. Moreover, the term poly(alkylstyrene) used here includes poly(methylstyrene), poly(ethylstyrene), poly(isopropylstyrene), poly(tert-butylstyrene), etc., and examples of poly(halostyrenes) include poly(chlorostyrene),  
20 poly(bromostyrene), and poly(fluorostyrene). Furthermore, examples of poly(alkoxystyrenes) include poly(methoxystyrene) and poly(ethoxystyrene). Among these substances, particularly preferred styrene polymers are polystyrene, poly(p-methylstyrene), poly(m-methylstyrene), poly(p-tert-butylstyrene), poly(p-chlorostyrene),  
25 poly(m-chlorostyrene), poly(p-fluorostyrene), and copolymers of styrene and p-methylstyrene.

Moreover, there are no particular restrictions on the molecular weight of the syndiotactic styrene polymer, but its weight average molecular weight should be 10,000 or above, and preferably 50,000 or above. If this weight average molecular weight is less than 10,000, chemical resistance will tend to be insufficient. Moreover, there are also no restrictions on the range of molecular weight distribution, and various ranges may be used. The syndiotactic styrene polymer has a melting point of 200-310°C, and its thermal resistance is outstanding compared with that of conventional styrene polymers having an atactic structure.

For example, this type of syndiotactic styrene polymer may be manufactured by polymerization of a styrene monomer (a monomer corresponding to the aforementioned styrene polymer), either in an inactive hydrocarbon solvent or without a solvent, using titanium or a condensation product of water and trialkyl aluminum as a catalyst (cf. Japanese Unexamined Patent Applications S62-104818, S63-268709), and commercial substances may also be used.

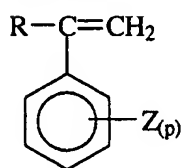
Furthermore, the syndiotactic styrene polymer may be modified using a modifier having a polar group. Examples include an acid hydride, carbonyl group, acid anhydride, acid amide, carboxylic ester, acid azide, sulfone group, nitrile group, cyano group, isocyanate ester, amino group, imide group, hydroxyl group, epoxy group, oxazoline group, or thiol group. Particularly preferred polar groups are acid anhydrides and epoxy groups, with a maleic anhydride group being preferred as an acid anhydride.

The high-impact styrene resin of component (C) used in the present invention is known in and of itself, and is obtained by graft

polymerization of an elastic body (rubber-like substance) and a portion of a styrene polymer. This [elastic body (rubber-like substance)/styrene resin] graft component is distributed in a stable manner when both molten and solid in the styrene resin in a form commonly referred to as a "salami" structure, with a size of approximately 0.1-4.0  $\mu\text{m}$ . High-impact styrene resin does not temporarily melt and disperse in molten plastic, unlike addition-type thermoplastic elastomer such as styrene-butadiene-styrene copolymer (SBS) and hydrogenated styrene-butadiene-styrene block copolymer (SEBS).

This high-impact styrene resin may be manufactured by any desired known polymerization method, such as that of dissolving an elastic body (rubber-like substance) in a styrene monomer. Polymerization may be carried out by the batch method or continuous method. Examples of polymerization methods include emulsion polymerization, bulk polymerization, and bulk suspension two-stage polymerization.

An example of the aforementioned styrene monomer is a monomer of General Formula (II) below:



in the above formula, R is a hydrogen atom or an alkyl group having 1-4 carbon atoms, Z is a halogen atom or a substituent which is an alkyl group having 1-4 carbon atoms, and p is an integer from 0 to 5.

Examples of the aforementioned elastic body (rubber-like substance) include polybutadiene, polyisoprene, butyl rubber, EPDM, ethylene-propylene copolymer, natural rubbers, and natural or

synthetic elastomers such as epichlorohydrin, with polybutadiene being preferred.

The high-impact styrene resin of component (C) should preferably be high-impact polystyrene (using styrene and polybutadiene).

5       The high-impact styrene resin of component (C) may be commercially obtained, with examples including the Dialex HT series marketed by Mitsubishi Kagaku K.K. and the Topalex series marketed by Mitsui Toatsu K.K.

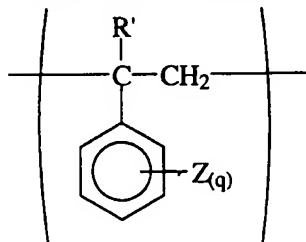
10       The aforementioned (A) PPE resin and (C) high-impact styrene resin should be blended in in the amounts of 90-10 parts by weight of (C) with respect to 10-90 parts by weight of (A), and preferably 80-10 parts by weight of (C) with respect to 20-90 parts by weight of (A). If the amount of (C) is too low, the effect of improving chemical resistance will not be achieved. Moreover, if the amount of (A) is too low, the outstanding  
15       properties of PPE resin will not be displayed.

20       Moreover, the syndiotactic styrene polymer of component (B) is mixed in in an amount of 5 to 60 parts by weight with respect to a total of 40 to 95 parts by weight of (A) and (C). Preferably, 10-50 parts by weight of (B) should be blended in with respect to a total of 90-50 parts by weight (A) and (C). Even more preferably, 15-50 parts by weight of (B) should be blended in with respect to a total of 85-50 parts by weight of (A) and (C). If the amount of the syndiotactic styrene polymer of component (B) is too high, dimensional accuracy and mechanical strength will decrease, and if it is too low, the effect of improving  
25       chemical resistance will not be achieved.



In addition to the above components, (D) a styrene resin may also be blended into the resin composition of the present invention as desired.

The styrene resin is known in and of itself, and this must be a  
 5 compound of General Formula (III) below:



in the formula, R' is a hydrogen atom or an alkyl group having 1-4 carbon atoms, Z' is a halogen atom or a substituent which is an alkyl group having 1-4 carbon atoms, and q is an integer from 0 to 5 in which  
 10 repeating structural units derived from vinyl aromatic compounds account for at least 25% by weight of the polymer. Examples of such styrene resins include homopolystyrene, styrene-containing copolymers such as styrene-methylstyrene copolymer, styrene-butadiene copolymer, styrene-acrylonitrile copolymer (SAN), styrene-maleic anhydride  
 15 copolymer, and styrene-acrylonitrile-butadiene copolymer (ABS). Homopolystyrenes include substances having an atactic or isotactic structure. Examples of styrene-class elastomers include styrene-butadiene copolymer (SBR), styrene-butadiene-styrene copolymer (SBS), hydrogenated styrene-butadiene-styrene block copolymer (SEBS),  
 20 styrene-isoprene copolymer (SIR), styrene-isoprene-styrene copolymer (SIS), and hydrogenated styrene-isoprene-styrene copolymer (SEPS). These styrene resins may be used either individually or in combinations of two or more. They may also be modified either partly or completely using a modifier having a polar group.

The styrene resin of component (D) should be blended in an amount of 50 parts by weight or less with respect to a total of 100 parts by weight of components (A), (B), and (C), and more preferably, 5-50 parts by weight.

- 5        In order to achieve the effect of the present invention, the resin composition should be such that  $\Delta E$ , which indicates the total degree of crystallization, satisfies the condition  $\Delta E < 54$ . More preferably, this should be  $\Delta E \leq 50$ .  $\Delta E$  is indicated by the Equation (i) below:

$$\Delta E (\%) = E_c / (E_{sp} \times W) \times 100 \quad (i)$$

- 10      in the above equation,  $E_c$  is the crystallization energy (unit: mJ/mg) of the resin composition measured with a differential scanning calorimeter;  $E_{sp}$  is the crystallization energy (unit: mJ/mg) of the syndiotactic styrene polymer alone measured under the same conditions as  $E_c$  above; and  $W$  is the weight ratio of the syndiotactic styrene
- 15      polymer in the resin composition. Thus  $\Delta E$  indicates the proportion of crystallization energy, which is a measure of the total degree of crystallization. Here,  $E_c$  is the crystallization energy (unit: mJ/mg) of the resin composition measured with a differential scanning calorimeter). The value of  $E_c$  is determined as follows: The molten resin
- 20      composition cools at a rate of  $-20^\circ\text{C}/\text{min}$ . in an inert gas atmosphere, its crystallization behavior is plotted, the area of the crystallization peaks obtained is determined, and this is taken as the crystallization energy ( $E_c$ ).  $E_{sp}$  is the crystallization energy (unit: mJ/mg) measured with the syndiotactic styrene polymer alone, and it is
- 25      measured under the same conditions as  $E_c$ .  $W$  is the weight ratio of the syndiotactic styrene polymer in the resin composition.

Moreover, in cases where a peak crystallization energy of the polymer composition cannot be obtained, i.e., cases in which the  $E_c$  value cannot be measured,  $E_c = 0$ , and the  $\Delta E$  value is also 0.

When the amount of the syndiotactic styrene polymer of component (B) blended in exceeds 60 parts by weight,  $\Delta E$  becomes 54% or higher, crystallization proceeds to an excessive degree during fabrication, adversely affecting dimensional accuracy due to molding shrinkage, and the composition becomes brittle, not only resulting in a decrease in mechanical properties such as impact strength, but bringing about a decrease in chemical resistance, despite the fact that there is a high proportion of crystal components. Moreover, in this type of mixing in an excess range, crystallization is accompanied by turbidity and opacity of the composition, causing the transparent amorphous properties of conventional modified polyphenylene ether resin to be lost.

Accordingly, when component (B) is present in the above-mentioned component range, i.e., when the condition of an  $\Delta E$  value  $< 54$  is satisfied, it is possible to achieve a sufficient improvement in chemical resistance for practical use without harming the properties of the polyphenylene ether resin composition, which is an amorphous resin, namely its high dimensional accuracy and other outstanding properties.

Moreover, in the present invention, various flame retardants may also be used. Examples include phosphoric ester flame retardants and halogen flame retardants. Among these, phosphoric ester flame retardants are preferred for safety reasons. Examples of phosphoric ester flame retardants include trimethylphosphate, triethylphosphate,

tributylphosphate, trioctylphosphate, tributoxyethylphosphate,  
triphenylphosphate, tricresylphosphate, cresylphenylphosphate,  
octyldiphenylphosphate, diisopropylphenylphosphate,  
tris(chloroethyl)phosphate, tris(chloropropyl)phosphate,  
5 tris(dichloropropyl)phosphate, bis(2,3-dibromopropyl)-2,3-  
dichloropropylphosphate, tris(2,3-dibromopropyl)phosphate, and  
polyphosphates such as (chloropropyl)monooctylphosphate, bisphenol A  
bisphosphate, hydroquinone bisphosphate, resorcinol bisphosphate, and  
trioxybenzene triphosphate, with triphenylphosphate and various  
10 polyphosphates being preferred.

In the resin composition of the present invention, moreover, in  
addition to the above components, one may add during mixing or molding  
of the resin, in amounts which do not impair the purpose of the  
invention, other resins, rubber-like substances (such as polybutadiene  
15 and polyisoprene; however, excluding styrene elastomers), common  
additives such as pigments, dyes, strengtheners (glass fibers, carbon  
fibers, etc.), fillers (carbon black, mica, talc, silica, titanium  
oxide, etc.), heat-resistance agents, antioxidants, weather-proofing  
agents, lubricants, mold-releasing agents, crystal nucleating agents,  
20 plasticizers, fluidity-improving agents, antistatic agents, and  
antibacterial and antifungal agents.

There are no particular restrictions on the method used for  
manufacturing the resin composition of the present invention, and any  
ordinary method may be used as appropriate. Generally speaking, the  
25 melt kneading method is preferred. Specific examples of equipment which  
may be used include extruders, Banbury mixers, rollers, and kneaders,  
and these may operate by either batch or continuous operation.

The resin composition of the present invention may be used to obtain the desired molded product in any desired form using any desired molding method, such as injection molding, extrusion molding, or blow molding.

5       The resin composition of the present invention should preferably meet the following conditions:

- (i) In a chemical resistance crack test carried out under strain conditions of 1% or above, it does not undergo cracking failure even when exposed to an organic substance selected from among fats and oils,  
10   grease, and organic solvents for 24 hours or more, and
- (ii) the molding shrinkage of a square plate test piece formed by injection molding (100 mm x 100 mm x 3 mm in thickness) is 0.8% or less in the flow direction and 0.8% or less in a direction perpendicular to the flow. Specific examples of the organic substance used in the 1.5%  
15   strain chemical resistance cracking test include tempura oil, salad oil, epoxy hardening agents, engine oil, gasoline, lubricating oil, wax remover solution, and rust-preventing agents.

#### EXAMPLES

20       The following is an explanation of the present invention in greater detail by means of working examples, but the present invention is not limited to these examples.

Moreover, in the working examples and comparison examples, the components used were as follows.

(A) Polyphenylene ether resin:

25       PPE: Poly(2,6-dimethyl-1,4-phenylene)ether having an intrinsic viscosity (chloroform, 25°C) of 0.48 dl/g manufactured by Nihon G.E. Plastics K.K.

(B) Syndiotactic polystyrene:

S-PS: trademark; Zarek 70Z (molecular weight 250,000, syndiotacticity indicated by racemic pentad ratio according to  $^{13}\text{C}$ -NMR analysis: 97%), manufactured by Shukko Sekiyu Kagaku Kogyo K.K.)

5 (C) High-impact styrene resin:

HIPS: High-impact polystyrene (trademark; HT644, manufactured by Mitsubishi Kasei K.K.)

(D) Styrene resin:

A-PS: General-purpose atactic polystyrene (trademark; CR3500,  
10 manufactured by Dainippon Inc. K.K.)

SBS: Styrene-butadiene-styrene copolymer, Kraton D1101CU  
(manufactured by Shell)

Working Examples 1-4 and Comparison Examples 1-11

(1) Extrusion process

15 The various components were mixed in the proportions (weight ratio) shown in Tables 1-2, and after being blended in a Henschel mixer, the mixture was melt-kneaded in a 30 mm biaxial extruder under conditions of set kneading temperature of 300°C and rotation speed of 300 rpm to obtain pellets.

20 (2) Molding process

Pellets obtained as described were injection-molded using an injection molding machine (manufactured by Toyo Kikai Kinzoku K.K., 80 tons) under conditions of set cylinder temperature of 300°C and mold temperature of 80°C to obtain test pieces.

25 Using the test pieces obtained, the following tests were conducted. The results are shown in Tables 1-2.

a: Chemical resistance test:

An extrusion-molded test piece measuring 3.2 mm x 12.7 mm x 63.5 mm was fixed in place on the forced 1.5% bending strain die shown in Fig. 1, and a chemical resistance test was conducted.

The following solvents were used:

- 5 \* Wax remover solution: Manufactured by Yushiro Kagaku Kogyo K.K., ST-7
- \* Epoxy hardening agent: Manufactured by Toshida Co., TCG1672
- \* Grease: Manufactured by Kyodo Yushi K.K., Multemp SRL
- \* Tempura oil: Manufactured by Showa K.K.
- \* Engine oil: Manufactured by Shell Premium, 5W30
- 10 \* Gasoline: Manufactured by Nihon Sekiyu K.K., regular gasoline
- \* Rust-preventing agent: Manufactured by Kure Kogyo K.K., CRC556

The test method was as follows:

- The test piece (3) was fixed in place on the bent portion of the 1.5% bending strain die (4), the surface of the curved portion of the
- 15 test piece was covered with gauze measuring 12.7 mm x 12.7 mm (1), a solvent (2) was dripped onto this gauze so as to saturate it, the time after dripping required for the test piece to rupture completely was measured, and this time was taken as a measure of chemical resistance. Test pieces which did not rupture after 24 hours were assessed as "No
- 20 break," and the test was concluded at that time. The reason is that in actual use, there are no applications which are subjected to the high strain of 1.5%, and a test duration of longer than 24 hours is considered unnecessary from a practical standpoint. Moreover, in cases where the solvent was grease, measurement was carried out after directly applying
- 25 the grease to the surface of the test piece.

The tests were conducted at the following temperatures:

In the case of grease, tempura oil, and engine oil, measurements were conducted in an air oven at 85°C, and in the case of wax remover solution, gasoline, the rust-preventing agent, and the epoxy hardening agent, because of the risk of fire due to the volatility of these  
5 substances, testing was conducted in a room temperature draft.

b: Measurement of molding shrinkage (evaluation of dimensional accuracy):

The flat plate test piece shown in Fig. 2, measuring 100 mm x 100 mm x 3 mm, was molded with a film gate (5) using the FAS-T100D molding  
10 machine manufactured by Fanac Co. (100 tons) under the same conditions as above (set cylinder temperature of 300°C and mold temperature of 80°C). The test pieces were first left standing for 24 hours at room temperature of 23°C and humidity of 50%, they were then measured five times in direction a and five times in direction b using a three-  
15 dimensional measuring device (AF211, manufactured by Mitsutoyo), and the average values were taken as the molding shrinkage flow direction (indicated by a in Fig. 2) and the direction parallel to the molding shrinkage flow (indicated by b in Fig. 2) respectively. Moreover, concerning the mold temperature for nylon molding, 60°C was selected  
20 as the general optimum condition in the case of non-addition, and for PPE/nylon alloy (Noryl GTX600), 80°C was selected as the general optimum condition in the case of non-addition.

c: Izod impact strength test:

A test piece obtained by injection molding measuring 3.2 mm x 12.7  
25 mm x 63.5 mm was measured for Izod impact strength using a notched test piece according to ASTM D-256.

d: HDT (heat distortion temperature):



A test piece obtained by injection molding measuring 6.4 mm x 12.7 mm x 63.5 mm was heated with a temperature increase rate of 2°C/min. in an oil tank according to ASTM D648 with a load of 18.6 kg, and heat distortion temperature was measured.

5 e: MI (melt flow index)

Measurements were conducted with a load of 10 kg at 250°C using a melt indexer manufactured by Takara K.K.

Table 1

	Working Example 1	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Working Example 2	Comparative Example 5	Comparative Example 6	Comparative Example 7
Ingredients (parts by weight)									
PPE	20	60	20	20	20	40	40	40	40
SBS	5	5	5	5	5	5	5	5	5
S-PS	40	40	-	40	80	30	-	30	60
A-PS	-	-	80	40	-	-	60	30	-
HIPS	40	-	-	-	-	30	-	-	-
Solvent resistance (wax remover)	No Break	7 hr. 12 min.	1min.	8 hr. 4 min.	No Break	No Break	2min.	6 hr. 14 min.	No Break
Solvent resistance (epoxy curing agent)	No Break	10 hr. 15 min.	1 min. 05 sec.	12 hr. 10 min.	No Break	No Break	1 min. 25 sec.	8 hr. 9 min.	No Break
Solvent resistance (grease)	No Break	12 hr. 01 min.	3hr. 42 min.	12 hr. 25 min.	No Break	No Break	6hr. 30 min.	14 hr. 20 min.	No Break
Solvent resistance (anti-corrosion agent)	No Break	8 hr. 32 min.	40 min. 20 sec.	7 hr. 18 min.	No Break	No Break	58 min. 40 sec.	6 hr. 32 min.	No Break
Solvent resistance (cooking oil)	No Break	11 hr. 25 min.	25 min. 10 sec.	14 hr.	No Break	No Break	40 min. 30 sec.	13 hr. 20 min.	No Break
Solvent resistance (engine oil)	No Break	11 hr. 47 min.	3hr. 50min.	10 hr. 10 min.	No Break	No Break	4hr. 13 min.	9 hr. 34 min.	No Break
Solvent resistance (gasoline)	No Break	2 hr. 03 min.	30sec.	2 hr. 46 min.	No Break	No Break	30 sec.	1 hr. 11 min.	No Break
IZOD impact resistance (kg-cm/cm)	13	9	12	11	10	13	11	11	12
HDT 18.6 kg load (°C)	105	140	105	105	106	125	126	125	125
MI 250°C, 10 kg load (g/10 min)	35	3	34	35	34	5	4.5	5	5
Mold shrinkage factor in direction of flow (%)	0.68	0.7	.69	0.68	1.02	0.67	0.67	0.68	0.92
Mold shrinkage factor perpendicular to flow (%)	0.69	0.68	0.68	0.69	1.23	0.67	0.68	0.68	1.1

Table 2

	Working Example 3	Comparative Example 8	Comparative Example 9	Working Example 4	Comparative Example 10	Comparative Example 11
Ingredients (parts by weight)						
PPE	60	60	60	80	80	80
SBS	5	5	5	5	5	5
S-PS	20	-	20	10	-	10
A-PS	-	40	20	-	20	10
HIPS	20	-	-	10	-	-
Solvent resistance (wax remover)	No Break	1 min. 30 min.	4hr.34 min.	No Break	1min.35sec.	4 hr. 24 min.
Solvent resistance (epoxy curing agent)	No Break	1 min. 20 sec.	11hr.8 min.	No Break	11 min. 30 sec.	11 hr. 18 min.
Solvent resistance (grease)	No Break	4hr. 21 min.	12hr.59min.	No Break	7hr.42min.	11 hr. 30 min.
Solvent resistance (anti-corrosion agent)	No Break	54hr.27min.	6hr.10min.	No Break	55 min.	13 hr. 22 min.
Solvent resistance (cooking oil)	No Break	45 min. 20 sec.	10hr.48min.	No Break	30 min. 20 sec.	14 hr. 29 min.
Solvent resistance (engine oil)	No Break	3hr.22 min.	9hr.48min.	No Break	2hr. 43 min.	14 hr. 30 min.
Solvent resistance (gasoline)	No Break	20 sec.	1hr.30min.	No Break	20 sec.	1 hr. 30 min.
IZOD impact resistance (kg-cm/cm)	12	10	11	8	8	8
HDT 18.6 kg load (°C)	140	143	142	164	163	163
MI 250°C, 10 kg load (g/10 min)	3	3	3	1	1	1
Mold shrinkage factor in direction of flow (%)	0.67	0.68	0.68	0.68	0.69	0.68
Mold shrinkage factor perpendicular to flow (%)	0.67	0.67	0.67	0.67	0.67	0.68

As can be seen from Table 1, in Comparison Example 1, the amount of syndiotactic polystyrene (S-PS) blended in was the same as in Working Example 1, but the PPE composition did not have high-impact polystyrene (HIPS) blended in. One can see that chemical resistance is extremely  
5 poor compared to Working Example 1.

Next, comparing Working Example 1 and Comparison Examples 2 and 3, in Comparison Example 2 (PPE/A-PS), in which the resin did not contain S-PS or HIPS, one can see that chemical resistance is markedly inferior. Moreover, in Comparison Example 3 (PPE/S-PS/A-PS), in which A-PS was  
10 blended in instead of HIPS, the effect of improving chemical resistance was superior to Comparison Example 2, but it was still markedly inferior to Working Example 1 (PPE/S-PS/HIPS). The same can be said for the comparisons of Working Example 2 with Comparison Examples 5 and 6, the comparisons of Working Example 3 with Comparison Examples 8 and 9 (Table  
15 2), and the comparisons of Working Example 4 with Comparison Examples 10 and 11 (Table 2). Thus it was found that by mixing S-PS with PPE, one can obtain an effect of improving chemical resistance, and when HIPS is included in the blend, one obtains a marked effect of improving chemical resistance. This effect is not obtained with a mixture of A-PS  
20 and S-PS. It is surprising that this chemical resistance-improving effect was obtained by blending in HIPS, which is used for improving impact resistance and is not thought to have anything to do with chemical resistance. Moreover, in all of the compositions of all of the working examples, characteristics such as mechanical strength and molding  
25 shrinkage (dimensional accuracy) were identical to PPE/A-PS.

Furthermore, in Comparison Examples 4 and 7, it can be seen that excessive amounts of S-PS were added, with chemical resistance being

observed which was identical to Working Examples 1 and 2 respectively, but the molding shrinkage was extremely high and dimensional accuracy was poor.

One can see that from the above that only when HIPS is combined  
5 with a specified amount of S-PS can one achieve a PPE resin composition showing outstanding chemical resistance while maintaining high dimensional accuracy.

The resin composition of the present invention makes it possible to markedly increase chemical resistance without impairing the inherent  
10 properties (particularly dimensional stability) of conventional polyphenylene ether resin (amorphous resin). Moreover, this advantage is not adversely affected by adding flame retardants or fillers (such as glass fibers and mica). Accordingly, the resin composition of the present invention is well-suited for applications in which such resins  
15 were previously limited, such as external automotive components, engine room components, and cabin interiors of ships, to which waxes, machine oils/engine oils, rust-preventing agents, aromatic agents, etc., may adhere, components for office equipment, computer-related equipment, etc., to which lubricating oils for sliding, grease, or cleaners may  
20 adhere (such as internal parts, fan motor cases, and plastic chassis); home electronic and commercial electrochemical product components, to which salad oil, tempura oil, or other organic solvents may adhere; and components of electrical and electronic equipment used in environments exposed to oil and smoke or organic gases (such as factory environments  
25 and construction environments). It is particularly well-suited for use in components subject to strain, and it is therefore extremely useful from an industrial standpoint.

## CLAIMS

1. A resin composition containing (A) a polyphenylene ether resin and (B) a syndiotactic styrene polymer, characterized in that

(1) the composition also contains (C) a high-impact styrene resin; and (2) the composition contains (C) in the amount of 90-10 parts by weight with respect to 10-90 parts by weight of (A) and (B) in the amount of 5 to 60 parts by weight with respect to a total of 40 to 95 parts by weight of (A) and (C).

2. Resin composition according to Claim 1, characterized by containing 80-20 parts by weight of (C) with respect to 20-80 parts by weight of (A).

3. Resin composition according to Claims 1 or 2, characterized by containing 10-50 parts by weight of (B) with respect to a total of 50-90 parts by weight of (A) and (C).

4. Resin composition according to any of Claims 1-3, characterized by also containing 50 parts by weight or less of (D) a styrene resin with respect to a total of 100 parts by weight of (A), (B), and (C).

5. Resin composition of any of Claims 1-4, characterized by simultaneously meeting the following conditions:

(i) in a chemical resistance crack test carried out under strain conditions of 1% or above, it does not undergo cracking failure even when exposed to an organic substance selected from among fats and oils, grease, and organic solvents for 24 hours or more, and

(ii) the molding shrinkage of a square plate test piece formed by injection molding (100 mm x 100 mm x 3 mm in thickness) is 0.8% or less in the flow direction and 0.8% or less in a direction perpendicular to the flow.

Fig. 1

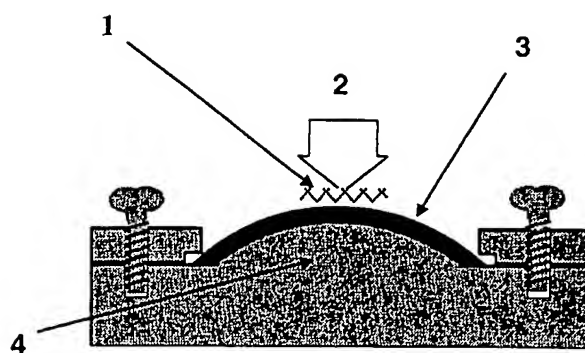
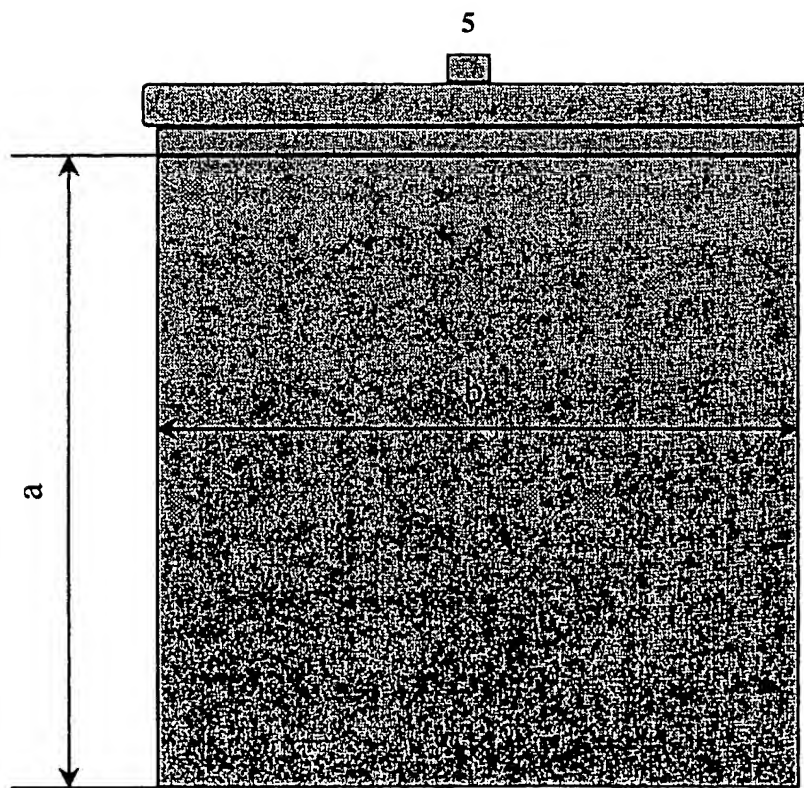


Fig. 2



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 98/05347

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C08L71/12 C08L25/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 356 857 A (IDEMITSU KOSAN CO) 7 March 1990 cited in the application see examples 14,17 see page 5, line 38 - line 41 see page 7, line 25 - line 30 ---	1-5
X	EP 0 422 495 A (IDEMITSU KOSAN CO) 17 April 1991 cited in the application *Comparative Example 4, Table 2* ---	1,3,5
A	EP 0 608 007 A (IDEMITSU KOSAN CO) 27 July 1994 see examples 13-15; table 2 --- -/--	1-5

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

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Date of the actual completion of the international search

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

O'Sullivan, T



# INTERNATIONAL SEARCH REPORT

Int .ional Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 585 (C-669), 22 December 1989 & JP 01 245052 A (SUMITOMO CHEM CO LTD), 29 September 1989 see abstract -----	1-5
A	EP 0 266 773 A (BORG WARNER CHEMICALS INC) 11 May 1988 see claim 1 see table 1 -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 98/05347

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0356857 A	07-03-1990	JP 2064140 A	05-03-1990
		JP 2765863 B	18-06-1998
		JP 2218724 A	31-08-1990
		JP 2636900 B	30-07-1997
		JP 2092948 A	03-04-1990
		JP 2824067 B	11-11-1998
		AT 114696 T	15-12-1994
		AT 159747 T	15-11-1997
		AU 623170 B	07-05-1992
		AU 4089689 A	08-03-1990
		DE 68919591 D	12-01-1995
		DE 68919591 T	13-04-1995
		DE 68928419 D	04-12-1997
		DE 68928419 T	26-02-1998
		EP 0611802 A	24-08-1994
		ES 2113003 T	16-04-1998
		FI 894030 A	01-03-1990
		KR 9606158 B	09-05-1996
		KR 9606160 B	09-05-1996
		US 5109068 A	28-04-1992
EP 0422495 A	17-04-1991	JP 3126743 A	29-05-1991
		JP 3126744 A	29-05-1991
		AU 628651 B	17-09-1992
		AU 6304690 A	18-04-1991
		CA 2027497 A	14-04-1991
		CN 1050886 A,B	24-04-1991
		EP 0608007 A	27-07-1994
		KR 118104 B	30-09-1997
		RU 2011665 C	30-04-1994
		RU 2066681 C	20-09-1996
		US 5219940 A	15-06-1993
		US 5777021 A	07-07-1998
EP 0608007 A	27-07-1994	JP 3126743 A	29-05-1991
		JP 3126744 A	29-05-1991
		AU 628651 B	17-09-1992
		AU 6304690 A	18-04-1991
		CA 2027497 A	14-04-1991
		CN 1050886 A,B	24-04-1991
		EP 0422495 A	17-04-1991
		KR 118104 B	30-09-1997
		RU 2011665 C	30-04-1994
		RU 2066681 C	20-09-1996
		US 5219940 A	15-06-1993
		US 5777021 A	07-07-1998
EP 0266773 A	11-05-1988	CA 1300784 A	12-05-1992
		JP 2665339 B	22-10-1997
		JP 63139939 A	11-06-1988
		US 4956497 A	11-09-1990